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Industrial lignins: the potential for efficient removal of Cr(VI) from wastewater

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Abstract

Cr(VI), a serious threat to human health, widely exists in the effluents of various industrial processes.. In this paper, the potential of industrial lignin for efficient removal of Cr(VI) from wastewater were systematically investigated, including pulping black liquor lignin (BLN), enzymolysis lignin (ELN), and SPORL pretreatment spent liquor (FS). The structure characterizations of three lignins were investigated by TG, FTIR, BET, SEM, and XPS. Among these three lignins, BLN showed the highest adsorption amount of Cr(VI) and best selectivity in wastewater simulation. According to the Langmuir model, the calculated maximum adsorption amount of Cr(VI) on ELN, BLN, and FS was 765.60, 880.57, and 721.58 mg g⁻¹, respectively. The adsorption of Cr(VI) by industrial lignins was a chemisorption process, during which Cr(VI) was reduced to low toxic Cr(III). This paper provided a promising application for the effective utilization of industrial lignins.

Keywords: Industrial Lignin; Cr(VI) Removal; Mechanism; Industrial wastewater

1. Introduction

Cr(VI), as a common heavy metal ion, is highly toxic, carcinogenic and non-degradable (Zhang et al. 2018). In the past few decades, Cr(VI) pollution has become a serious problem. Cr(VI) not only pollutes water (Gan et al. 2015), it can also accumulate in fish and other aquatic animals, causing serious harm to humans (Ge & Li 2018). Hence, the removal of Cr(VI) has always been the focus of researchers' attention. Among the various technologies of removing Cr(VI), adsorption is an efficient and economical technology, since different kinds of adsorbents with low cost can be prepared and used (Wang & Chen 2009). Using biomass as an adsorbent, also called biosorption (Kesaano & Sims 2014, Kwak et al. 2015), will be an inexpensive alternative to existing commercial activated carbon.

Lignin, the second largest natural polymer after cellulose, is a highly branched and complex polymer. It contains p-hydroxybenzene (H), guaiacyl (G) and syringyl (S) phenylpropane units, while the composition and quantity of the units vary with the species of plants and industrial processes. In addition, the functional groups, such as methoxy, phenolic hydroxyl, aliphatic hydroxyl, benzyl alcohol, non-cyclic phenyl ether, and carbonyl, have a significant influence on the reaction characteristics of lignin (Chen & Wan 2017, Ralph et al. 2019, Xu et al. 2006). At present, the major sources of lignin available for large-scale application are from the pulp and paper making industry and cellulosic ethanol industry (Lauwaert et al. 2019).

It is well known that pulping black liquor is a toxic and badly stained pulp wastewater. Its color and toxicity have a negative impact on water resources, and it contains a large amount of lignin, which is difficult to be degraded naturally (Fu et al.

2013, Gao et al. 2013). Lignin can be separated and purified from pulping black liquor by using its special performance in acid-base environment, which can not only treat black liquor friendly, but also bring secondary economic value. Biorefining of biomass for generating biofuels and high valued chemicals has attracted increasing research interest (Zhou et al. 2016b). During the biorefining process, different lignin by-products are produced, such as enzymolysis lignin and lignins in pretreatment spent liquor. However, most of the industrial lignins are directly burned or wantonly discharged (Zhao et al. 2020b). After appropriate modification, industrial lignin can be used as adsorbent (Zhou et al. 2020), dispersant (Zhou et al. 2015), water reducing agent (Zhou et al. 2016a), and rubber reinforcing agent (Gregorová et al. 2006). Unfortunately, although the utilization of lignin is widely concerned, the comprehensive utilization ratio of lignin is less than 5% (Li et al. 2015).

In this study, the potential of industrial lignins for efficient removal of Cr(VI) from aqueous solution were investigated. Three different types of lignins, namely pulping black liquor lignin (BLN), enzymolysis lignin (ELN), and SPORL pretreatment spent liquor (FS), were employed as adsorbents. The structure characterizations of three lignins were investigated by TGA, FTIR, SEM, BET, and XPS. The removal efficiency and adsorption performance for Cr(VI) of these three lignins were systematically studied, including: i) the effect of adsorption time, original metal concentration, and temperature on adsorption process; ii) adsorption isotherm, thermodynamics, and kinetics; iii) wastewater simulation, Cr species changes during adsorption, and potential adsorption mechanism.

2. Materials and methods

2.1 Materials

Pulping black liquor was come from a kraft pulping process. Enzymolysis lignin was kindly provided by Shandong Longlive Bio-technology CO., Ltd. (Shandong, China). Pulping black liquor lignin (BLN) and enzymolysis lignin (ELN) was purified using HCl precipitation method. Briefly, 10 g of samples were dissolved in 50 g deionized water at pH=12 using NaOH adjustment. After stirring evenly, the mixture was filtered by vacuum to remove insoluble impurities. The filtrate was collected. After adjusting the pH to 2.0, the slurry was kept stirring at 75 °C for 2 h. Then distilled water was used to wash the solid until the pH was stable. The BLN or ELN was obtained by filtration and then dried at 60 °C. Lignin sulfonate was produced from the SPORL pretreatment liquor of Douglas-fir, denoted as FS. The details of the FS production could be found in our previous study (Zhou et al. 2018). Sym-Diphenylcarbazine and acetone were supplied by Kelon Chemical Co., Ltd. (Chengdu, China). Other chemicals, such as $K_2Cr_2O_7$, HCl, NaOH, Na_3PO_4 , Na_2SO_4 , $Al(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, H_2SO_4 , H_3PO_4 were analytically pure.

2.2 Characterization

The surface area and pore structure of adsorbents were measured by a surface area analyzer (ASAP 2460, Micromeritics) at 77 K. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area (S_{BET}). According to the single point adsorption of N_2 , the total volume (V_{tot}) could be obtained. A thermogravimetric analyzer (Mettler TGA 2, Swiss) was used to analyze the thermal stability of the adsorbents under a N_2 flow (50 mL min^{-1}) from room temperature to 900 °C. FTIR was investigated by the KBr disk method using a Nicolet iS50 FTIR (Liang et al. 2020b). The

FTIR spectrum was taken in a wavelength between 400 and 4000 cm^{-1} . The surface characteristics of adsorbents were measured by a scanning electron microscopy (SEM) (Apreo, FEI, Hillsboro, USA), operated at the acceleration voltage of 2.0 kV. XPS was measured on a VG ESCALAB 250XI spectrometer (Thermo Electron) with an Al $K\alpha$ (1486 eV) X-ray source.

2.3 Adsorption of Cr(VI)

Cr(VI) solutions with different concentrations were prepared from various weights of $\text{K}_2\text{Cr}_2\text{O}_7$. At pH=2, the effects of adsorption temperature (25-45 $^{\circ}\text{C}$), contact time (0-72 h) and Cr(VI) concentration (800-1600 mg L^{-1}) on the adsorption were investigated. HCl solution was used to adjust the pH of the solution. The ambient temperature and rotational speed during the adsorption process were controlled by a constant temperature shaker. 50 mg of adsorbent was added into 50 mL Cr(VI) solution during all adsorption experiments. After a certain period of time, 1 mL of solution was taken out and centrifuged at 10000 rpm for 3 min. The supernatant was collected and diluted. The Cr(VI) concentration was determined at 542 nm with a UV-2450 (Shimadzu Co.).

Removal rate $R(\%)$ and adsorption quantity q_t (mg g^{-1}) can be calculated by the following formulas:

$$R(\%) = \frac{C_0 - C_t \times n}{C_0} \times 100\% \quad (1)$$

$$q_t = \frac{(C_0 - C_t \times n) \times V}{m} \quad (2)$$

Where, C_0 represents the original Cr(VI) concentration (mg L^{-1}), C_t represents Cr(VI) concentration (mg L^{-1}) after adsorption at time t, and n represents the dilution multiple.

To understand the form of chromium in solution after adsorption, a flame atomic absorption spectrophotometer was used (TAS 986F, Beijing Purkinje General Instrument Co., Ltd.) to determine total chromium concentration. The difference between the total chromium and Cr(VI) concentration was the Cr(III) concentration. The adsorption process was performed at 35 °C with Cr(VI) initial concentration of 800 mg L⁻¹.

3 Results and Discussion

3.1 Structural characterization analysis

3.1.1 BET analysis

Table 1 Porous structure parameters of ELN, BLN, and FS.

Sample	S_{BET} (m ² g ⁻¹)	V_{tot} (cm ³ g ⁻¹)	V_{mic} (cm ³ g ⁻¹)	V_{ext} (cm ³ g ⁻¹)	D_{P} (nm)
ELN	29.78	0.2697	-0.0033	0.2697	36.23
BLN	11.65	0.0129	-0.0035	0.0129	4.44
FS	8.53	0.0061	-0.0035	0.0061	2.86

Fig.1. Pore size distributions of ELN (a), BLN (b) and FS (c).

The S_{BET} , V_{tot} and D_{P} of the three adsorbents were listed in Table 1. Fig.1 showed the pore size distributions diagram measured by the DFT method. Among the three adsorbents, the S_{BET} of ELN (29.78 m² g⁻¹) was the largest, and that of BLN and FS was 11.65 and 8.53 m² g⁻¹, respectively. As observed Fig.1, all adsorbents almost had no micropores, which could be also demonstrated by the values of V_{mic} (Table 1). Different from ELN, the pore width of BLN and FS were mainly concentrated in the mesoporous

range, while ELN contained a large number of macropores. The D_P of ELN was 36.23 nm, with the V_{tot} of $0.2967 \text{ cm}^3 \text{ g}^{-1}$. The D_P of BLN was 4.44 nm with the V_{tot} of $0.0129 \text{ cm}^3 \text{ g}^{-1}$, while that of FS was 2.86 nm and $0.0061 \text{ cm}^3 \text{ g}^{-1}$, respectively. In general, the high surface area and abundant pores are beneficial for the adsorption capacity of materials (Yi et al. 2019).

3.1.2 TGA analysis

Fig.2. TGA curves of ELN, BLN and FS.

The TGA curves of three lignins were illustrated in Fig. 2. All TGA curves could be roughly divided into three stages (Cha et al. 2020, Chen et al. 2019, Dhyani & Bhaskar 2018, Li et al. 2020): (1) When the temperature increased from 30 to 158 °C, the mass of lignin decreased slightly, which was mainly attributed to the loss of water. (2) The rapid decrease of lignin mass at 158-660 °C resulted from the rapid decomposition of lignin polymer structure to form a variety of volatile compounds, such as aromatic hydrocarbons, phenols. (3) The temperature range between 660-900 °C was defined as a slow phase of thermal decomposition due to the formation of a highly dense aromatic structure which might be converted into coke. The maximum decomposition rates of

ELN, BLN and FS was at 375 °C, 377 °C and 299 °C, respectively. The terminal mass loss of ELN and BLN was 59.98% and 61.01%, while that of FS was 41.44%, indicating that the thermal stability of FS was the best among the three adsorbents.

3.1.3 FTIR

Fig.3. FTIR of ELN, BLN and FS.

According to Fig.3, the three lignins contained some of the same functional groups, such as O-H at 3422 cm^{-1} , symmetric and asymmetric C-H stretching vibrations of methyl and methylene at 2934, 2842 and 1458 cm^{-1} (Popovic et al. 2020, Qi et al. 2016), and characteristic peaks of aromatic ring at 1614, 1510 and 1423 cm^{-1} (Luo et al. 2018). All three lignins represented characteristic peaks of syringyl at around 1330, 1114, and 830 cm^{-1} , and guaiacyl at 1270 and 1150 cm^{-1} (Zhao et al. 2020b). The intensity of the syringyl ring breathing with C-O stretching at 1330 cm^{-1} was highest for BLN (Dai et al.

2017). The peak at 1700 cm^{-1} was attributed to the carbonyl groups, the intensity of which in FS was lowest. The phenolic OH and ether could be founded at 1213 cm^{-1} (Tejado et al. 2007). This peak in BLN was sharp, while it was unconspecious in FS. The peak at 1040 cm^{-1} was typical of primary alcohol C-O (Pan et al. 2016). After chromium ion was adsorbed, the spectra of the three lignins changed greatly. The C-H stretching vibrations, phenolic OH, C-O stretching and carbonyl groups almost disappeared. In addition, new peaks, assigned to the adsorbed chromium ions, appeared at 930 and 544 cm^{-1} (S.K. Das 2008, Y.G. Ko 2002).

3.1.4 SEM

Fig.4. SEM images of ELN, BLN, FS before (a, b, c), after (d, e, f) Cr(VI) adsorption,

and Cr mapping images (g, h, i) after adsorption.

The SEM images of raw ELN, BLN and FS were quite different (Fig.4 (a, b, c)). The surface of the ELN exhibited honeycomb-like holes, therefore, it possessed the largest surface area among these three lignins. BLN had a smooth surface with multiple spheres without cracks. The FS surface was relatively flat with some ravines. The SEM images of the three adsorbents were in agreement with the S_{BET} data. The EDS spectra of the three lignins were shown in Fig.S1 and Fig.4 (g, h, i). All three lignins contained C, H, and O elements. Except these elements, BLN and FS also contained S elements. After adsorption, there were significant Cr signal on all three lignins surface. However, there was no significant difference between the SEM images of ELN and BLN before and after Cr adsorption (Fig. 4(a) and (d), Fig. 4(b) and (e), respectively). However, the SEM image of FS after adsorption of Cr was different from the original FS. Plenty of particles were gathered on the surface of FS after Cr adsorption (Fig. 4(f)).

3.1.5 XPS

Fig.5. XPS survey spectra of ELN (a), BLN (b) and FS (c) before and after Cr adsorption.

Fig.6. XPS spectra of C1s before and after Cr adsorption by ELN (a), BLN (b) and FS (c).

Fig.7. XPS spectra of O1s before and after Cr adsorption by ELN (a), BLN (b) and FS (c).

Fig.8. XPS spectra Cr 2p after Cr adsorption by ELN, BLN and FS.

Fig.5 showed that the three adsorbents all contained elements of C and O. In addition, BLN and FS also contained S element. This phenomenon was consistent with the EDS results. After the completion of adsorption, Cr was detected on all three adsorbents. By comparing the C 1s and O 1s spectra before and after the adsorption (Fig.6 and Fig.7), it can be seen that functional groups related to C and O played a non-negligible role in Cr(VI) removal. Taking ELN as an example, the C 1s XPS spectrum of ELN (Fig.6 (a)) exhibited three peaks (Chen et al. 2018, Djellabi et al. 2019, Ma et al. 2014), which were C-C (53.3%, graphite) at 284.7 eV, C-O (33.9%, alcohol, phenolic hydroxyl and/or ether) at 286.2 eV, and C=O (12.8%, carbonyl and/or quinone) at 288.2 eV, respectively. After the adsorption of Cr, the proportion of C-O at 286.2 eV decreased to 24.6%, and the proportion of C=O at 288.2 eV increased to 17.2%. It indicated that C-O might be oxidized to C=O during the adsorption process. Similarly, according to Fig.6 (b) and (c), the proportion of C-O in BLN and FS decreased from 38.5%

and 42.6% before adsorption to 21.1% and 28.8% after adsorption, respectively, while the proportion of C=O increased from 5.6%, 5.1% to 17.1%, 14.6%, respectively. The high-resolution of O1s XPS spectrum proved this phenomenon. As shown in Fig.7, the O1s spectrum before the adsorption was deconvoluted into three peaks, including C-O, O-C=O, and C=O at 533.5, 532.5, and 531.4 eV, respectively (Chen et al. 2020, Li et al. 2017). After Cr adsorption, the proportion of C=O in ELN, BLN and FS changed from 12.7%, 13.7% and 37.7% to 57.0%, 55.7%, 56.8%, respectively. These changes might be due to oxidation of C-O, especially for ELN and BLN (Qi et al. 2016, Zhao et al. 2020a). The proportion of C-O in ELN and BLN decreased from 27.99%, 31.09% to 3.57%, 4.52%, respectively. Furthermore, the proportion of O-C=O was also decreased, which might be attributed to the complexation between O-C=O and Cr. A new peak at 529.9 eV assigned to Cr-O was detected (Shi et al. 2020). According to Fig. 8, the Cr 2p spectra after adsorption of all adsorbents indicated that Cr was existed in two forms: Cr (VI) and Cr (III) (Guo et al. 2017, Zhang et al. 2015). The existence of low-toxic Cr(III) suggested the reduction of highly toxic Cr(VI). In Cr 2p 3/2 and Cr 2p 1/2, the total proportions of Cr(III) adsorbed by ELN, BLN and FS were 58.3%, 41.7% and 62.7%, respectively. This indicated that the three adsorbents had a certain adsorption capacity of Cr(III).

3.2 Adsorption of Cr(VI)

3.2.1 Effect of time

Fig.9. Effect of time on adsorption of Cr(VI) on BLN, ELN and FS: (a) time - adsorption capacity diagram; (b) time - removal rate diagram.

FS showed a rapid adsorption characteristic at the early moment of adding adsorbents to Cr(VI) solution (Fig.9). After 30 min of adsorption, the removal rate of Cr(VI) by ELN and BLN reached 10.6% and 7.2%, and the adsorption capacity was 63.8 and 43.1 mg g⁻¹, respectively. However, the removal rate of Cr(VI) by FS reached 19.2%, moreover, the adsorption quantity was 114.9 mg g⁻¹. It indicated the important role of C-O functional groups on FS surface in the early stage of adsorption. With the extension of time, the removal rate gradually slowed down, which was related to the weakening of active sites and mass transfer impetus. The adsorption capacity of the three adsorbents gradually rose. After 4320 min of adsorption, the three adsorbents reached adsorption equilibrium. The removal rate of ELN, BLN and FS was 85.0%, 99.4% and 63.2%, respectively. The adsorption capacity was 509.8, 596.7 and 379.7 mg g⁻¹, respectively. Although ELN had the largest S_{BET} among these three adsorbents, the adsorption amount of ELN was smaller than that of BLN. It indicated that the role of functional groups was more important during Cr(VI) adsorption, such as phenolic hydroxyl groups.

3.2.2 Effect of initial metal concentration

Fig.10. Effect of different concentrations (a:1000 mg L⁻¹; b:1200 mg L⁻¹; c:1400 mg L⁻¹) on the adsorption capacity of ELN, BLN and FS.

According to Fig.10, with increasing Cr(VI) concentration, the adsorption amount of the three adsorbents increased. When the concentration rose from 1000 to 1400 mg L⁻¹, the adsorption capacity of ELN, BLN and FS increased from 589.2, 697.0 and 443.9 mg g⁻¹ to 626.2, 758.8 and 482.8 mg g⁻¹, respectively. The increased content of Cr(VI) in solution enhanced the driving force between adsorbates and adsorbents, and thus improved the adsorption capacity. Similarly, no matter at what concentration, the adsorption capacity of BLN was always the largest, while that of FS was the smallest. However, at the early moment of the adsorption, FS exhibited the fastest removal rate of Cr(VI). This result was in accordance with that in the previous section.

3.2.3 Effect of temperature

Fig.S2 showed the effect of temperature on adsorption at different concentrations. It could be seen that the increment of temperature contributed to the enhancement of adsorption capacity. When the adsorption temperature increased from 25 °C to 45 °C, the adsorption capacity of Cr(VI) on ELN, BLN and FS increased from 610.6, 731.1, and 427.0 mg g⁻¹ to 710.6, 774.7, and 582.1 mg g⁻¹, with the increasement of 100, 43.6, and 155.1 mg g⁻¹, respectively. The adsorption quantity of BLN for Cr(VI) was almost

independent of the adsorption temperature, while the adsorption quantity of ELN, especially FS, was highly dependent on the adsorption temperature. At higher temperature, the vibration frequency of Cr(VI) was enhanced, which was beneficial for the collision between lignins and Cr(VI). Moreover, the higher temperature might promote the transfer of electrons from lignins to Cr(VI), resulting in the reduction of Cr(VI) (Chi et al. 2020).

3.2.4 Study of Cr species during adsorption

Fig.11. The variation trend of total Cr, Cr(VI) and Cr(III) in solution during ELN (a), BLN (b) and FS (c) adsorption.

Under 35 °C and pH 2.0, the variation trend of the total Cr, Cr(VI) and Cr(III) in solution with time was investigated at initial Cr(VI) concentration of 800 mg L⁻¹. After 4320 min adsorption, the removal rate of Cr(VI) by ELN, BLN and FS was 71.8%, 84.3%, and 52.1%, respectively (Fig.11). The total chromium residual rate after ELN, BLN and FS adsorption was 44.3%, 15.0% and 62.4%, while the Cr(III) residual amount

accounted for 36.4%, 33.0% and 23.3% of the total chromium residual amount. The concentrations of Cr(III) in solution were 128.8, 39.6 and 116.1 mg L⁻¹, after ELN, BLN and FS adsorption, respectively (Fig.S3). This fully demonstrated that the three adsorbents could reduce Cr(VI) into Cr(III), although their reduction capacity was different. It was worth noting that Cr(III) was detected at 300 min and 600 min for FS adsorption process, with the content of 129.7 and 141.9 mg L⁻¹, respectively. With the extension of adsorption time, the concentration of Cr(III) first decreased to 75.9 mg L⁻¹ and then steadily increased to 116.1 mg L⁻¹. It indicated that FS might have a strong adsorptive reduction ability at the early stage of the adsorption, which effectively reduced Cr(VI) into less toxic Cr(III). This might result in the great influence of temperature change on Cr(VI) adsorption by FS. Cr(VI) and Cr(III) competed for limited active sites on the surface of FS, which might be one of the reasons for the weak adsorption ability of FS. In terms of ELN and BLN, especially BLN, there was no Cr(III) was detected in the solution at the initial adsorption stage.

3.2.5 Adsorption isotherm

The adsorption isotherm was used to provide insight into the affinity or driving force between the adsorbate and adsorbent (Mushtaq et al. 2016). Two of the most commonly used adsorption isotherm models, Langmuir and Freundlich, were used to study the adsorption process (Naushad et al. 2019).

Langmuir adsorption model presumes that adsorption occurs at a specific homogeneous adsorption site within the adsorbent (Tomczyk et al. 2020). Once a molecule occupies an adsorption site, no further equilibrium saturation point of adsorption will occur (Foo & Hameed 2010). In other words, the adsorption process is

single-layer adsorption. Its expression is:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where q_m means the maximum monolayer adsorption capacity of Cr(VI) (mg g^{-1}), (mg g^{-1}) and K_L means the Langmuir constant, which has relation to the affinity between the adsorbate and adsorbent (L mg^{-1}). C_e is the residual concentration of adsorbate in solution (mg L^{-1}), q_e means the quantity of adsorbate adsorbed by a unit mass of adsorbent at equilibrium (mg g^{-1}). Dimensionless constant R_L , also known as the separation factor, is often used to describe the basic features of the Langmuir adsorption model:

$$R_L = \frac{1}{1 + K_L \times C_o} \quad (4)$$

R_L suggests the adsorption tendency: $R_L = 0$ (irreversible); $R_L > 1$ (unfavorable); $R_L = 1$ (linear); and $0 < R_L < 1$ (favorable) (Martins et al. 2015).

The Freundlich model is more comprehensive, which described multilayer adsorption on heterogeneous surfaces. Its assumption takes into account the molecular interaction between the adsorbate and the adsorbent (Antunes et al. 2017). Its expression is as follows:

$$q_e = K_F \times C_e^{\frac{1}{n}} \quad (5)$$

Where K_F and n are the Freundlich rate constants designated as adsorption capacity (L g^{-1}) and adsorption intensity, respectively. The value of $1/n$ gives an indication of the favorability of adsorption. If $1 > 1/n > 0$, it suggests that the removal of metal ions is beneficial (Li et al. 2018).

Fig.12. Isotherm model fitting of Cr(VI) adsorption on adsorbents: (a) ELN, (b) BLN, (c) FS.

The adsorption isotherms at different temperatures of the three adsorbents were studied, and the fitting results were illustrated in Fig.12. The fitting parameters of the two isothermal models could be found in Table S1 and Table S2. The isotherms of the three adsorbents were in line with the Langmuir model, because their fitting correlation coefficient R^2 was closer to 1. It indicated that the Cr(VI) adsorption on all the three adsorbents was in single molecular layer. The R_L value was between 0 and 1, indicating that ELN, BLN and FS were favorable for Cr(VI) adsorption. Besides, the smaller the R_L value is, the higher the affinity between lignin and Cr is (Ma et al. 2019). Among the

three lignins investigated, BLN showed the smallest R_L values. At the range of investigated initial concentrations (700-1700 mg L⁻¹), the R_L values declined from 0.0015 to 0.0006, 0.0011 to 0.0005, and 0.0010 to 0.0004, at 25, 35, and 45 °C, respectively. At 45 °C and pH=2, the maximum monolayer adsorption capacity of ELN, BLN and FS was 765.60, 880.57 and 721.58 mg g⁻¹, respectively.

3.2.6 Adsorption thermodynamics

Thermodynamic parameters can be calculated by the equilibrium constant as a function of temperature (Yadav et al. 2013). Gibbs free energy change (ΔG^0), entropy change (ΔS^0), and enthalpy change (ΔH^0), were calculated by the following equations:

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (6)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (7)$$

where K_d (mL g⁻¹) means the thermodynamic equilibrium constant, R means the gas constant (J mol⁻¹ K⁻¹), T (K) represents the absolute temperature. The plots of K_d versus $1/T$ was illustrated in Fig. S4. The calculated thermodynamic parameters were reported in Table 2. The ΔG^0 of the three adsorbents was negative, indicating that the adsorption processes were spontaneous. Furthermore, the ΔG^0 declined with increasing temperature, suggesting that the higher the temperature was, the better the adsorption efficiency was. The positive value of ΔH^0 indicated the endothermic property of the adsorption process. It was proved that increasing temperature was conducive to the adsorption process (Yadav et al. 2013). The ΔS^0 value was positive, indicating that the randomness of the solid solution interface increased (Singha & Das 2011).

Table 2 Thermodynamic constants for the adsorption of Cr(VI) on the three adsorbents at

various temperatures.

Adsorbents	T/K	K _d	$\Delta G^0/\text{kJ mol}^{-1}$	$\Delta H^0/\text{kJ mol}^{-1}$	$\Delta S^0/\text{J mol}^{-1} \text{ K}^{-1}$	R ²
ELN	298	1.706	-4.229	36.581	126.955	0.9812
	308	2.550	-6.533			
	318	4.322	-11.433			
BLN	298	4.928	-12.215	5.066	30.263	0.9459
	308	5.363	-13.741			
	318	5.601	-14.816			
FS	298	0.886	-2.196	20.576	67.842	0.9613
	308	1.089	-2.789			
	318	1.495	-3.953			

3.2.7 Adsorption kinetics

For understanding the mass transfer and rate-controlling mechanism during the adsorption process, the kinetic data fitting was investigated by pseudo-first-order and pseudo-second-order kinetic model. Their expressions are as follows (Bhatti et al. 2020):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

where q_e and q_t (mg g^{-1}) mean the adsorption capacity at equilibrium and time t (min), respectively. k_1 (min^{-1}) and k_2 (g (mg min)^{-1}) are the pseudo-first-order and pseudo-second-order equilibrium rate constant, respectively.

Fig.13. Pseudo-first-order kinetic model fitting of Cr(VI) adsorption on adsorbents: (a) ELN, (b) BLN, (c) FS.

Fig.14. Pseudo-second-order kinetic model fitting of Cr(VI) adsorption on adsorbents: (a) ELN, (b) BLN, (c) FS.

The fitting curves of the two dynamics models were illustrated in Fig.13 and Fig.14. The kinetic parameters under different conditions were summarized in Table S3 and Table S4. By comparing the data in Table S3 and Table S4, no matter which adsorbent was used, the adsorption was more consistent with pseudo-second-order kinetic model, because the R^2 of the second-order kinetic model was larger ($R^2 > 0.995$). This results indicated that the process rate-controlling was mainly due to the chemisorption, in which the adsorbent and the absorbate were connected by electron sharing or electron exchange (Yadav et al. 2013).

3.2.8 Wastewater simulation

In wastewater treatment, coexisting ions might compete with Cr(VI) for active sites. Hence, it is necessary to investigate the competitive influence of coexisting anions and cations on Cr(VI). The influence of single coexisting ion (Cu^{2+} , Ni^{2+} , Al^{3+} , Cl^- , SO_4^{2-} , PO_4^{3-}) and their mixtures on Cr(VI) removal was investigated at a concentration of 600 mg L^{-1} . For the mixtures, the total concentration of coexisting ions was 3600 mg L^{-1} .

Fig.15. Effects of coexisting ions Cr(VI) removal by ELN (a), BLN (b) and FS (c).

As observed in Fig.15, on the whole, the presence of coexisting ions had a certain inhibitory effect on Cr(VI) removal, especially for ELN. The selectivity of BLN for Cr(VI) was the best among the three lignins. The existence of cations had no influence on Cr(VI) removal by BLN. After blending different ions (total ions concentration of 3600 mg L^{-1}) into simulated industrial wastewater, the removal rate of Cr(VI) still remained at a high level, only dropping from 99.6% to 92.6% after 48 h adsorption. Coexisting ions

also had little effect on Cr(VI) removal by FS, and the removal rate decreased by about 7.1% after 3600 mg L⁻¹ ions addition. However, ELN showed the worst selectivity of Cr(VI). The removal rate of Cr(VI) dropped from 87.2% to 63.0% after 3600 mg L⁻¹ ions addition. After 48 h adsorption, the adsorption amount of Cr(VI) by ELN was 371.47 mg g⁻¹, while it was 340.32 mg g⁻¹ by FS. Among all cations studied, Al³⁺ exhibited higher inhibition. Ni²⁺ and Cu²⁺ almost had no effect on Cr(VI) removal rate by three lignins. In terms of anions, the effect of SO₄²⁻ was largest, which might be due to its similar ionic radius with HCrO₄⁻. Moreover, bivalent anion might exhibit stronger electrostatic interaction. However, the influence of PO₄³⁻ on Cr(VI) removal rate was lower than that of SO₄²⁻. One possible reason was that PO₄³⁻ might be hydrolyzed into HPO₄²⁻, H₂PO₄⁻ and H₃PO₄ in solution, making the actual charge of PO₄³⁻ lower than that of SO₄²⁻ (Liang et al. 2020a, Lin et al. 2019). To sum up, the three lignins studied have good adsorption potentials for Cr(VI) and applicability in industrial wastewater.

3.3 Potential adsorption mechanism

Based on the above discussion, the potential adsorption mechanism of Cr(VI) by three lignins were illustrated in Fig.16. The lignins with abundant functional groups, such as carboxyl and hydroxyl groups, could effectively adsorb Cr(VI) from aqueous solution through electrostatic attraction or complexation. Then, Cr(VI) was reduced to Cr(III) with the assistance of electron-donor groups. The possible reduction was shown in Eq.(10-11). The produced Cr(III) could be partially immobilized through complexation or precipitation.

Fig.16. The possible mechanism diagrams of Cr (VI) adsorption on lignin.

4. Conclusion

Removal efficiency of Cr(VI) by different industrial lignins were systematically compared in this study. Among these three lignins, BLN exhibited the largest adsorption capacity of Cr(VI), while that of FS was smallest. According to the adsorption kinetics and thermodynamics study, Langmuir model and pseudo-second-order kinetic model could well explain the adsorption of Cr(VI) by the adsorbent. In this process, the increase of temperature was conducive to the improvement of adsorption capacity. According to the Langmuir model, the maximum monolayer adsorption amount of ELN, BLN and FS was 765.60, 880.57, and 721.58 mg g⁻¹ at 45 °C and pH=2, respectively. During the wastewater simulation experiment, BLN showed the optimal selectivity of Cr(VI), and FS was the medium. After blending different ions (total ions concentration of 3600 mg/L) into simulated industrial wastewater, the removal rate of Cr(VI) only dropped from 99.6% to 92.6% after 48 h adsorption. The adsorption of Cr(VI) on three lignins was a chemisorption process, during which Cr(VI) was reduced to Cr(III) with low toxicity.

Therefore, industrial lignin has a broad application prospect for heavy metal adsorption.

Declarations

- Ethics approval and consent to participate

Not applicable.

- Consent for publication

Not applicable.

- Availability of data and materials

Not applicable.

- Competing interests

The authors declare that they have no competing interests.

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- Authors' contributions

H. Zhang completed the overall design of the experiment and completed the first draft of the manuscript; H. Zhou provided key ideas for the experiment, and completed writing-reviewing and editing of the article, as well as the financial support.

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Figures

Figure 1

Pore size distributions of ELN (a), BLN (b) and FS (c).

Figure 2

TGA curves of ELN, BLN and FS.

Figure 3

FTIR of ELN, BLN and FS.

Figure 4

SEM images of ELN, BLN, FS before (a, b, c), after (d, e, f) Cr(VI) adsorption, and Cr mapping images (g, h, i) after adsorption.

Figure 5

XPS survey spectra of ELN (a), BLN (b) and FS (c) before and after Cr adsorption.

Figure 6

XPS spectra of C1s before and after Cr adsorption by ELN (a), BLN (b) and FS (c).

Figure 7

XPS spectra of O1s before and after Cr adsorption by ELN (a), BLN (b) and FS (c).

Figure 8

XPS spectra Cr 2p after Cr adsorption by ELN, BLN and FS.

Figure 9

Effect of time on adsorption of Cr(VI) on BLN, ELN and FS: (a) time - adsorption capacity diagram; (b) time - removal rate diagram.

Figure 10

Effect of different concentrations (a:1000 mg L⁻¹; b:1200 mg L⁻¹; c:1400 mg L⁻¹) on the adsorption capacity of ELN, BLN and FS.

Figure 11

The variation trend of total Cr, Cr(VI) and Cr(III) in solution during ELN (a), BLN (b) and FS (c) adsorption.

Figure 12

Isotherm model fitting of Cr(VI) adsorption on adsorbents: (a) ELN, (b) BLN, (c) FS.

Figure 13

Pseudo-first-order kinetic model fitting of Cr(VI) adsorption on adsorbents: (a) ELN, (b) BLN, (c) FS.

Figure 14

Pseudo-second-order kinetic model fitting of Cr(VI) adsorption on adsorbents: (a) ELN, (b) BLN, (c) FS.

Figure 15

Effects of coexisting ions Cr(VI) removal by ELN (a), BLN (b) and FS (c).

Figure 16

The possible mechanism diagrams of Cr (VI) adsorption on lignin.

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